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Analytical solutions for non-equilibrium solute transport in three-dimensional porous media

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Abstract

The movement of water and chemicals in soils is generally better described with multidimensional non-equilibrium models than with more commonly used one-dimensional and/or equilibrium models. This paper presents analytical solutions for non-equilibrium solute transport in semi-infinite porous media during steady unidirectional flow. The solutions can be used to model transport in porous media where the liquid phase consists of a mobile and an immobile region (physical non-equilibrium) or where solute sorption is governed by either an equilibrium or a first-order rate process (chemical non-equilibrium). The transport equation incorporates terms accounting for advection, dispersion, zero-order production, and first-order decay. General solutions were derived for the boundary, initial, and production value problems with the help of Laplace and Fourier transforms. A comprehensive set of specific solutions is presented using Dirac functions for the input and initial distribution, and/or Heaviside or exponential functions for the input, initial, and production profiles. A rectangular or circular inflow area was specified for the boundary value problem while for the initial and production value problems the respective initial and production profiles were located in parallelepipedal, cylindrical, or spherical regions of the soil. Solutions are given for both the volume-averaged or resident concentration as well as the flux-averaged or flowing concentration. Examples of concentration profiles versus time and position are presented for selected problems. Results show that the effects of non-equilibrium on three-dimensional transport are very similar to those for one-dimensional transport.

Introduction

Many experimental and theoretical studies have been undertaken to improve the understanding, management, and prediction of the movement of dissolved substances in soils. These investigations are primarily motivated by concerns about possible contamination of the subsurface environment. Although several uncertainties still exist, and probably will remain for some time, regarding the correct description of water and solute transport processes

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in field soils, subsurface solute transport is generally described with the advection-dispersion equation (ADE). In the deterministic approach, explicit closed-form solutions for the transport problem can often be derived if the model parameters are constant with respect to time and position. One-dimensional solutions of the ADE have been widely reported for equilibrium transport (e.g. Van Genuchten and Alves, 1982) and to some extent for non-equilibrium transport (Lassey, 1988; Van Genuchten and Wagenet, 1989). In spite of the fact that many transport problems are multidimensional, relatively few analytical solutions have been reported for two- and three-dimensional transport (e.g. Wexler, 1989), particularly for non-equilibrium transport (Goltz and Roberts, 1986). This is surprising since such analytical solutions can be deduced quite easily from one-dimensional solutions.

Goltz and Roberts (1986) provided analytical solutions for two-region-type mobile-immobile models applicable to transport from an instantaneous point source in an infinite porous medium made up of rectangular, cylindrical, or spherical aggregates. Transport between the two regions was governed by a first-order rate expression. Analytical solutions for the concentration distribution inside the soil aggregate were obtained by solving Fick's law for diffusion assuming different aggregate geometries. The solutions by Goltz and Roberts (1986) are applicable to transport involving horizontal flow in infinite aquifers. An alternative, and equally common, pollution scenario involves downward flow from the soil surface. The semi-infinite nature of such a transport system makes the solution slightly more complicated, but also more general than the infinite case treated by Goltz and Roberts. Since the size and geometry of soil aggregates is poorly defined for field problems, no attempt is made to solve the more complicated problem for solute transport in a porous medium consisting of idealized aggregates.

The problem to be investigated here is of a very similar nature to, but more comprehensive than, the equilibrium case outlined by Leij et al. (1991). The solution procedure is based on previous work for one-dimensional non-equilibrium transport assuming a first-order rate exchange (Van Genuchten and Wagenet, 1989; Toride et al., 1993) and multidimensional transport (Leij et al., 1991). The objective of this paper is to combine these two approaches and to provide a relatively concise set of solutions of the three-dimensional non-equilibrium ADE for a wide variety of boundary, initial, and production value problems.

For clarity of presentation both the 'chemical' and 'physical' non-equilibrium models will be formulated. These models will be cast in the same dimensionless form for subsequent mathematical analysis. After outlining the general solution procedure, analytical solutions are presented for the equilibrium and non-equilibrium concentrations as volume- and flux-

averaged types. General solutions will be given for: (1) the boundary value problem (BVP) with an arbitrary solute input, which depends on time and transverse spatial coordinates; (2) the initial value problem (IVP) using an arbitrary initial distribution, which depends on all three spatial coordinates; (3) the production value problem (PVP) based on an arbitrary production profile, which depends on time and the three spatial coordinates. Although the general solutions are relatively inconvenient for further use, they can be greatly simplified for some practical input, initial, and production profiles described by Dirac, Heaviside, or exponential functions.

Model description

Solute movement in an isotropic soil during one-dimensional downward flow and with three-dimensional dispersion is modeled analytically by assuming that both the velocity and the dispersion coefficients are constant with respect to time and space. These assumptions are approximate but may be adequate for many applications. Furthermore, solutes are assumed to be subject to linear retardation (i.e. equilibrium sorption between solution and sorbed phases can be described with a linear isotherm), and zero- and first-order production or degradation processes. Non-equilibrium is attributed to differences in exchange sites (assuming equilibrium sorption for ‘type-1’ and non-equilibrium sorption for ‘type-2’ sites), or to mobile and immobile fluid regions (Van Genuchten and Wagenet, 1989).

In the two-site model, non-equilibrium sorption for type-2 sites is typically described with a first-order rate law (Selim et al., 1976; Cameron and Klute, 1977). The governing equations for this ‘chemical’ non-equilibrium model may be written as

$$\begin{aligned}
 \left(1 + \frac{f\rho k}{\theta}\right) \frac{\partial c}{\partial t} &= D_x \frac{\partial^2 c}{\partial x^2} - \nu \frac{\partial c}{\partial x} + D_y \frac{\partial^2 c}{\partial y^2} + D_z \frac{\partial^2 c}{\partial z^2} \\
 &- \frac{\alpha\rho}{\theta} [(1-f)kc - s_k] - \mu_1 c - \frac{f\rho k\mu_{s,e}}{\theta} c + \lambda_1(x, y, z, t) \\
 &+ \frac{f\rho\lambda_{s,e}(x, y, z, t)}{\theta}
 \end{aligned} \tag{1a}$$

$$\frac{\partial s_k}{\partial t} = \alpha[(1-f)kc - s_k] - \mu_{s,k} s_k + (1-f)\lambda_{s,k}(x, y, z, t) \tag{1b}$$

where c is the volume-averaged solute concentration in the liquid phase (ML^{-3}), s_k is the concentration in the sorbed phase for type-2 sites

(MM⁻¹); t is time (T); x is position (L) in the direction of flow; y and z are rectangular coordinates perpendicular to the flow direction (L), i.e. parallel to the soil surface; D_x is a dispersion coefficient (L²T⁻¹) in the x direction (i.e. representing longitudinal dispersion); D_y and D_z are transverse dispersion coefficients in the y and z directions, respectively; θ is the volumetric water content (L³L⁻³); v is the macroscopically averaged downward pore-water velocity (LT⁻¹); f is the fraction of type-1 exchange sites, ρ is the bulk density (ML⁻³); k is a distribution coefficient for linear sorption (ML⁻³), α is a first-order kinetic rate coefficient (T⁻¹); μ_l and μ_s are first-order decay coefficients for degradation in the liquid and sorbed phases, respectively (T⁻¹); λ_l (ML⁻³T⁻¹) and λ_s (MM⁻¹T⁻¹) are time- and position-dependent zero-order rate coefficients for solute production in the liquid and sorbed phases, respectively; while the subscripts e and k refer to equilibrium and kinetic exchange sites, and l and s refer to the liquid and sorbed phases.

The 'physical' non-equilibrium model assumes that the liquid region can be partitioned into mobile (or flowing) and immobile (or stagnant) regions, that solute movement occurs by advection and dispersion in the mobile region, and that solute exchange between the two regions occurs by first-order diffusion (Coats and Smith, 1964; Van Genuchten and Wierenga, 1976). The governing equations for the two-region model are

$$\begin{aligned}
 (\theta_m + f\rho k) \frac{\partial c_m}{\partial t} = & \theta D_x \frac{\partial^2 c_m}{\partial x^2} - \theta v \frac{\partial c_m}{\partial x} + \theta D_y \frac{\partial^2 c_m}{\partial y^2} + \theta D_z \frac{\partial^2 c_m}{\partial z^2} - \alpha(c_m - c_{im}) \\
 & - (\theta_m \mu_{l,m} + f\rho k \mu_{s,m}) c_m + \theta_m \lambda_{l,m}(x, y, z, t) + f\rho \lambda_{s,m}(x, y, z, t)
 \end{aligned} \quad (2a)$$

$$\begin{aligned}
 [\theta_{im} + (1-f)\rho k] \frac{\partial c_{im}}{\partial t} = & \alpha(c_m - c_{im}) - [\theta_{im} \mu_{l,im} + (1-f)\rho k \mu_{s,im}] c_{im} \\
 & + \theta_{im} \lambda_{l,im}(x, y, z, t) + (1-f)\rho \lambda_{s,im}(x, y, z, t)
 \end{aligned} \quad (2b)$$

where in this case represents the fraction of sorption sites in equilibrium with the fluid of the mobile region and a is a first-order mass transfer coefficient (T⁻¹); the subscripts m and im refer to the mobile and immobile liquid regions, respectively, with $\theta = \theta_m + \theta_{im}$.

The two-site and the two-region models can be cast in the same dimensionless form using the parameters listed in Table 1. Notice that several parameters in Table 1 are expressed in terms of an arbitrary characteristic

Table 1
Dimensionless parameters for the two-site and two-region transport models

Parameter	Two-site model	Two-region model
T	$\frac{\nu t}{L}$	$\frac{\nu t}{L}$
<i>X, Y, Z</i>	$\frac{x}{L}, \frac{y}{L}, \frac{z}{L}$	$\frac{x}{L}, \frac{y}{L}, \frac{z}{L}$
<i>P_x, P_y, P_z</i>	$\frac{\nu L}{D_x}, \frac{\nu L}{D_y}, \frac{\nu L}{D_z}$	$\frac{\nu L}{D_x}, \frac{\nu L}{D_y}, \frac{\nu L}{D_z}$
β	$\frac{\theta + f\rho k}{\theta + \rho k}$	$\frac{\theta_m + f\rho k}{\theta + \rho k}$
R	$1 + \frac{\rho k}{\epsilon}$	$1 + \frac{\rho k}{\epsilon}$
<i>w</i>	$\frac{\alpha(1 - \beta)RL}{\nu}$	$\frac{\alpha L}{\theta\nu}$
<i>C₁</i>	$\frac{c}{c_0}$	$\frac{c_m}{c_0}$
<i>C₂</i>	$\frac{s_k}{(1 - f)kc_0}$	$\frac{c_{im}}{c_0}$
<i>μ₁</i>	$\frac{L}{\theta\nu}(\theta\mu_1 + f\rho k\mu_{s,e})$	$\frac{L}{\theta\nu}(\theta_m\mu_{1,m} + f\rho k\mu_{s,m})$
<i>μ₂</i>	$\frac{L}{\theta\nu}[(1 - f)\rho k\mu_{s,k}]$	$\frac{L}{\theta\nu}[\theta_{im}\mu_{1,im} + (1 - f)\rho k\mu_{s,im}]$
<i>λ₁</i>	$\frac{L}{\theta\nu c_0}(\theta\lambda_1 + f\rho\lambda_{s,e})$	$\frac{L}{\theta\nu c_0}(\theta_m\lambda_{1,m} + f\rho\lambda_{s,m})$
<i>λ₂</i>	$\frac{L}{\theta\nu c_0}[(1 - f)\rho\lambda_{s,k}]$	$\frac{L}{\theta\nu c_0}[\theta_{im}\lambda_{1,im} + (1 - f)\rho\lambda_{s,im}]$

concentration, *c*₀, and characteristic length, *L*. The following dimensionless model can be obtained (see also Nkedi-Kizza et al., 1984)

$$\beta R \frac{\partial C_1}{\partial T} = \frac{1}{P_x} \frac{\partial^2 C_1}{\partial X^2} - \frac{\partial C_1}{\partial X} + \frac{1}{P_y} \frac{\partial^2 C_1}{\partial Y^2} + \frac{1}{P_z} \frac{\partial^2 C_1}{\partial Z^2} + \omega(C_2 - C_1) - \mu_1 C_1 + \lambda_1(X, Y, Z, T) \tag{3a}$$

$$(1 - \beta)R \frac{\partial C_2}{\partial T} = \omega(C_1 - C_2) - \mu_2 C_2 + \lambda_2(X, Y, Z, T) \tag{3b}$$

where *β* is a partition coefficient, *R* is a retardation factor, *C*₁ and *C*₂ are equilibrium and non-equilibrium resident concentrations, respectively, *T* is time; *X* is the longitudinal coordinate; *Y* and *Z* are transverse coordinates;

P_x, P_y and P_z are the Peclet numbers in the X, Y and Z directions; ω is a mass transfer coefficient; μ and λ are dimensionless first-order decay and zero-order production terms; and the subscripts 1 and 2 refer to the equilibrium and non-equilibrium phases, respectively. The magnitude of several dimensionless parameters in Eq. (3a,b) depends not only on the dimensional model parameters but also on the arbitrary constants c_0 and \mathbf{L} . Unless specified otherwise, we assume that the solute concentration is of the volume-averaged or resident concentration type.

The initial and boundary conditions for Eq. (3) are

$$C_1(X, Y, Z, 0) = C_2(X, Y, Z, 0) = f(X, Y, Z) \quad (4)$$

$$\left(C_1 - \frac{1}{P_x} \frac{\partial C_1}{\partial X} \right) \Big|_{X=0^+} = g(Y, Z, T) \quad (5a)$$

$$\frac{\partial C_1}{\partial X}(\infty, Y, Z, T) = 0 \quad (5b)$$

$$C_1(X, \pm\infty, Z, T) = 0 \quad \frac{\partial C_1}{\partial Y}(X, \pm\infty, Z, T) = 0 \quad (6a, b)$$

$$C_1(X, Y, \pm\infty, T) = 0 \quad \frac{\partial C_1}{\partial Y}(X, Y, \pm\infty, T) = 0 \quad (7a, b)$$

where f and g are arbitrary functions which will be specified later, along with λ , to illustrate pertinent transport problems. Because advective-dispersive transport occurs exclusively in phase 1, the boundary conditions are only cast in terms of C_1 . The linearity of the problem enables us to solve the boundary (BVP), initial (IVP), and production (PVP) value problems separately. In the BVP it is assumed that λ_1 and λ_2 in Eq. (3) and $g(Y, Z, T)$ in Eq. (5a) are equal to zero. The IVP is solved by dropping the production terms, λ , and by setting $f(X, Y, Z)$ equal to zero. The PVP requires that the input function, $g(Y, Z, T)$, and the initial distribution, $f(X, Y, Z)$, are set to zero.

Concentrations obtained from the effluent of finite soil columns or from solution samplers are usually viewed as representing the equilibrium concentration, C_1 . On the other hand, soil coring or non-destructive techniques such as TDR or electrical conductivity will give total concentrations, i.e. those defined as mass of solute per unit volume of soil, with weighted contributions from both the equilibrium (C_1) and non-equilibrium (C_2) phases according to

$$C_T = \beta R C_1 + (1 - \beta) R C_2 \quad (8)$$

The injection and detection mode for several solute displacement experiments may require the use of flux-averaged or flowing concentrations (Kreft and Zuber, 1978; Parker and Van Genuchten, 1984). They can be obtained by substituting the analytical expression for the resident concentration, C or C^r , obtained for a third-type inlet condition, into the well-known transformation

$$C^f = C^r - \frac{1}{P_x} \frac{\partial C^r}{\partial x} \tag{9}$$

This equation can be readily applied if the expression for C^r is differentiable with respect to X and if the flow field is uniform, i.e. having a constant Peclet number.

General solutions

The solution of Eq. (3), subject to Eqs. (4)-(7) was obtained using Laplace transforms with respect to X and T , and a double Fourier transform with respect to Y and Z . This approach was discussed previously by Leij et al. (1991), among others. Further information regarding the use of integral transforms can be found in Spiegel (1965) and Sneddon (1972). The solution of the non-equilibrium three-dimensional ADE is tedious but relatively straightforward. Details regarding the derivation of all presented analytical solutions are available from the senior author upon request. The inverse Laplace transform with respect to X utilizes the shifting property, the convolution theorem, and a table of Laplace transforms. Subsequently, the last remaining boundary condition (Eq. 5b) is used in conjunction with Leibnitz' rule for differentiation of an integral. The Laplace inversion with respect to T is carried out by using the property that the iterated Laplace transform of a function is equal to the ordinary Laplace transform of the generalized convolution integral of this function (De Smedt and Wierenga, 1979a; Walker, 1987). This method was applied by Lindstrom and Narasimhan (1973) to derive the solutions for an initial value problem involving non-equilibrium sorption. The inverse Fourier transformation constituted the last step of the solution procedure.

For an arbitrary input function, $g(Y, Z, T)$ the general solution to the BVP, C^B , is

$$C_1^B = \int_0^T \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} g(Y - \phi, Z - \Omega, T - \tau) \left[\exp\left(-\frac{\omega\tau}{\beta R}\right) \Gamma_1(\phi, \Omega, \tau) G^B(X, \tau) + \int_0^{\tau} \sqrt{\frac{\alpha\eta}{\tau - \eta}} H_1(\eta; \tau) \Gamma_1(\phi, \Omega, \eta) G^B(X, \eta) d\eta \right] d\Omega d\phi d\tau \tag{10a}$$

Table 2
Expressions for auxiliary longitudinal term, $G(X, \tau)$, in the general and specific solutions to the BVP, IVP, and PVP for resident and flux concentrations

G	Resident concentration (C^r)	Flux concentration (C^f)
$G^B(X, \tau)$	$\exp\left(-\frac{\mu_1\tau}{\beta R}\right) \left\{ \sqrt{\frac{P_x}{\pi\beta R\tau}} \exp\left[-\frac{(\beta RX - \tau)^2}{4\beta R\tau/P_x}\right] - \frac{P_x}{2\beta R} \exp(P_x X) \operatorname{erfc}\left(\frac{\beta RX + \tau}{\sqrt{4\beta R\tau/P_x}}\right) \right\}$	$\sqrt{\frac{\beta R P_x X^2}{4\pi\tau^3}} \exp\left[-\frac{\mu_1\tau}{\beta R} - \frac{(\beta RX - \tau)^2}{4\beta R\tau/P_x}\right]$
$G^I(X, \tau)$ $G^P(X, \tau)$	$\exp\left(-\frac{\mu_1\tau}{\beta R}\right) \left(\sqrt{\frac{\beta R P_x}{4\pi\tau}} \exp\left\{P_x X - \frac{[\beta R(\xi + X) + \tau]^2}{4\beta R\tau/P_x}\right\} - \frac{P_x}{2} \exp(P_x X) \operatorname{erfc}\left[\frac{\beta R(\xi + X) + \tau}{\sqrt{4\beta R\tau/P_x}}\right] + \sqrt{\frac{\beta R P_x}{4\pi\tau}} \exp\left\{-\frac{[\beta R(\xi - X) + \tau]^2}{4\beta R\tau/P_x}\right\} \right)$	$\sqrt{\frac{\beta R P_x}{4\pi\tau}} \exp\left(-\frac{\mu_1\tau}{\beta R}\right) \left(\left[1 - \frac{\beta R(\xi - X) + \tau}{2\tau}\right] \times \exp\left\{-\frac{[\beta R(\xi - X) + \tau]^2}{4\beta R\tau/P_x}\right\} - \left[1 - \frac{\beta R(\xi + X) + \tau}{2\tau}\right] \times \exp\left\{P_x X - \frac{[\beta R(\xi + X) + \tau]^2}{4\beta R\tau/P_x}\right\} \right)$
$G_1^I(X, \tau; X_i)$ $G_1^P(X, \tau; X_i)$	$\exp\left(-\frac{\mu_1\tau}{\beta R}\right) \left(1 - \frac{1}{2} \operatorname{erfc}\left[\frac{\beta R(X - X_i) - \tau}{\sqrt{4\beta R\tau/P_x}}\right] + \frac{1}{2} \left[1 + P_x(X + X_i) + \frac{P_x\tau}{\beta R} \right] \exp(P_x X) \times \operatorname{erfc}\left[\frac{\beta R(X + X_i) + \tau}{\sqrt{4\beta R\tau/P_x}}\right] - \sqrt{\frac{P_x\tau}{\pi\beta R}} \times \exp\left\{P_x X - \frac{[\beta R(X + X_i) + \tau]^2}{4\beta R\tau/P_x}\right\} \right)$	$\exp\left(-\frac{\mu_1\tau}{\beta R}\right) \left\{ 1 - \frac{1}{2} \operatorname{erfc}\left[\frac{\beta R(X - X_i) - \tau}{\sqrt{4\beta R\tau/P_x}}\right] - \frac{1}{2} \exp(P_x X) \operatorname{erfc}\left[\frac{\beta R(X + X_i) + \tau}{\sqrt{4\beta R\tau/P_x}}\right] - \sqrt{\frac{\beta R}{4\pi\tau P_x}} \exp\left(-\frac{[\beta R(X - X_i) - \tau]^2}{4\beta R\tau/P_x}\right) + \sqrt{\frac{\beta R}{4\pi\tau P_x}} \exp\left(P_x X - \frac{[\beta R(X + X_i) + \tau]^2}{4\beta R\tau/P_x}\right) \right\}$

$$\begin{aligned}
 G_2^I(X, \tau; \gamma_I) & \exp \left[(\gamma_{I/P} + \gamma_{I/P}^2/P_x - \mu_1) \frac{\tau}{\beta R} \right] & \left(1 + \frac{\gamma_{I/P}}{P_x} \right) \exp \left[(\gamma_{I/P} + \gamma_{I/P}^2/P_x - \mu_1) \frac{\tau}{\beta R} \right] \\
 G_2^P(X, \tau; \gamma_P) & \times \left(\exp(-\gamma_{I/P} X) \left\{ 1 - \frac{1}{2} \operatorname{erfc} \left[\frac{\beta R X - \tau(1 + 2\gamma_{I/P}/P_x)}{\sqrt{4\beta R \tau/P_x}} \right] \right\} \right) & \times \left(\exp(-\gamma_{I/P} X) \left\{ 1 - \frac{1}{2} \operatorname{erfc} \left[\frac{\beta R X - \tau(1 + 2\gamma_{I/P}/P_x)}{\sqrt{4\beta R \tau/P_x}} \right] \right\} \right) \\
 & + \frac{1}{2} (1 + P_x/\gamma_{I/P}) \exp[(\gamma_{I/P} + P_x)X] & + \frac{1}{2} \exp[(\gamma_{I/P} + P_x)X] \\
 & \times \operatorname{erfc} \left[\frac{\beta R X + \tau(1 + 2\gamma_{I/P}/P_x)}{\sqrt{4\beta R \tau/P_x}} \right] & \times \operatorname{erfc} \left\{ \frac{\beta R X + \tau(1 + 2\gamma_{I/P}/P_x)}{\sqrt{4\beta R \tau/P_x}} \right\} \\
 & - \frac{P_x}{2\gamma_{I/P}} \exp \left(P_x X - \frac{\mu_1 \tau}{\beta R} \right) \operatorname{erfc} \left(\frac{\beta R X + \tau}{\sqrt{4\beta R \tau/P_x}} \right) &
 \end{aligned}$$

Table 3
Expressions for auxiliary non-equilibrium terms, H , and transverse terms, Γ , in the general and specific solutions to the BVP, IVP, and PVP

H or Γ	Expression
$H_0(\tau; T)$	$\exp\left[-\frac{\omega\tau}{\beta R} - \frac{\omega + \mu_2}{(1 - \beta)R}(T - \tau)\right] I_0[2\sqrt{a(T - \tau)\tau}]$
$H_1(\tau; T)$	$\exp\left[-\frac{\omega\tau}{\beta R} - \frac{\omega + \mu_2}{(1 - \beta)R}(T - \tau)\right] I_1[2\sqrt{a(T - \tau)\tau}]$
$\Gamma_1(Y, Z, \tau)$	$\frac{\beta R \sqrt{P_y P_z}}{4\pi\tau} \exp\left[-\frac{\beta R(P_y Y^2 + P_z Z^2)}{4\tau}\right]$
$\Gamma_2(Y, Z, \tau)$	$\frac{1}{4} \operatorname{erfc}\left(\sqrt{\frac{\beta R P_y}{4\tau}} Y\right) \operatorname{erfc}\left(\sqrt{\frac{\beta R P_z}{4\tau}} Z\right)$
$\Gamma_3(Y, Z, \tau; Y_i, Z_i)$	$\frac{1}{4} \left\{ \operatorname{erf}\left[\frac{\beta R P_y}{4\tau}(Y_i + Y)\right] + \operatorname{erf}\left[\sqrt{\frac{\beta R P_y}{4\tau}}(Y_i - Y)\right] \right\} \left\{ \operatorname{erf}\left[\frac{\beta R P_z}{4\tau}(Z_i + Z)\right] + \operatorname{erf}\left[\sqrt{\frac{\beta R P_z}{4\tau}}(Z_i - Z)\right] \right\}$
$\Gamma_4(Y, Z, \tau; r_i)$	$\frac{1}{4} \int_{Y-r_i}^{Y+r_i} \sqrt{\frac{\beta R P_y}{\pi\tau}} \exp\left(-\frac{\beta R P_y \phi^2}{4\tau}\right) \left(\operatorname{erfc}\left\{\sqrt{\frac{\beta R P_z}{4\tau}}\left[Z - \sqrt{r_i^2 - (Y - \phi)^2}\right]\right\} \right. \\ \left. - \operatorname{erfc}\left\{\sqrt{\frac{\beta R P_z}{4\tau}}\left[Z + \sqrt{r_i^2 - (Y - \phi)^2}\right]\right\} \right) d\phi$
$\Gamma_5(Y, Z, \tau; X_0, r_i)$	$\frac{1}{4} \int_{X_0-r_i}^{X_0+r_i} G^{1/P}(\xi, \tau) \int_{Y-\sqrt{r_i^2 - (\xi - X_0)^2}}^{Y+\sqrt{r_i^2 - (\xi - X_0)^2}} \sqrt{\frac{\beta R P_y}{\pi\tau}} \exp\left(-\frac{\beta R P_y \phi^2}{4\tau}\right) \left(\operatorname{erfc}\left\{\sqrt{\frac{\beta R P_z}{4\tau}}\left[Z - \sqrt{r_i^2 - (\xi - X_0)^2 - (Y - \phi)^2}\right]\right\} \right. \\ \left. - \operatorname{erfc}\left\{\sqrt{\frac{\beta R P_z}{4\tau}}\left[Z + \sqrt{r_i^2 - (\xi - X_0)^2 - (Y - \phi)^2}\right]\right\} \right) d\phi d\xi$

$$C_2^B = \frac{\omega}{(1 - \beta)R} \int_0^T \exp \left[-\frac{\omega + \mu_2}{(1 - \beta)R} (T - \tau) \right] C_1^B(X, Y, Z, \tau) d\tau \tag{10b}$$

where the auxiliary function $G^B(X, \tau)$ is given in Table 2 and the functions $\Gamma_1(\phi, \Omega, \tau)$ and $H_1(\eta; \tau)$ are given in Table 3, in which I_1 denotes the first-order modified Bessel function. Furthermore, the variable a in Eq. (10a) and Table 2 is defined as

$$a = \omega^2[\beta(1 - \beta)R^2] \tag{11}$$

The longitudinal dependency of the solution is completely contained in the term G^B . This feature allows for a convenient transformation of the resident solution, C^r , of the problem described by Eqs. (3)–(7), to the flux-averaged mode, C^f , according to Eq. (9). Table 2 contains expressions for $G^B(X, \tau)$ which can be used to obtain both concentration modes.

Similarly, the solution to the IVP, C^I , for a yet unspecified initial distribution $f(X, Y, Z)$ is

$$\begin{aligned} C_1^I = & \int_0^\infty \int_{-\infty}^\infty \int_{-\infty}^\infty f(\xi, Y - \phi, Z - \Omega) \left[\exp \left(-\frac{\omega T}{\beta R} \right) \Gamma_1(\phi, \Omega, T) G^I(X, T) \right. \\ & \left. + \int_0^T \left[\frac{\omega}{\beta R} H_0(\tau; T) + \sqrt{a\tau/(T - \tau)} H_1(\tau; T) \right] \right. \\ & \left. \times \Gamma_1(\phi, \Omega, \tau) G^I(X, \tau) d\tau \right] d\Omega d\phi d\xi \end{aligned} \tag{12a}$$

$$\begin{aligned} C_2^I = & f(X, Y, Z) \exp \left(-\frac{\omega + \mu_2}{(1 - \beta)R} T \right) + \frac{\omega}{(1 - \beta)R} \\ & \times \int_0^\infty \int_{-\infty}^\infty \int_{-\infty}^\infty \int_0^T f(\xi, Y - \phi, Z - \Omega) \left[H_0(\tau; T) + \frac{\omega}{\beta R} \sqrt{\frac{T - \tau}{a\tau}} H_1(\tau; T) \right] \\ & \times \Gamma_1(\phi, \Omega, \tau) G^I(X, \tau) d\tau d\Omega d\phi d\xi \end{aligned} \tag{12b}$$

where $H_0(\tau; T)$ is also given in Table 3 in which I_0 is the zero-order modified Bessel function.

Finally, the equilibrium and non-equilibrium concentrations for the general PVP are

$$\begin{aligned} C_1^P = & \frac{1}{\beta R} \int_0^\infty \int_{-\infty}^\infty \int_{-\infty}^\infty \int_0^T \left[\mathbf{J}(p, q) \lambda_1(\xi, Y - \phi, Z - \Omega, T - \tau) \right. \\ & \left. + \frac{\omega}{\omega + \mu_2} [1 - \mathbf{J}(q, p)] + \lambda_2(\xi, Y - \phi, Z - \Omega, T - \tau) \right] \exp \left[-\frac{\omega \mu_2 \tau}{(\omega + \mu_2) \beta R} \right] \\ & \times \Gamma_1(\phi, \Omega, \tau) G^P(X, \tau) d\tau d\Omega d\phi d\xi \end{aligned} \tag{13a}$$

$$\begin{aligned}
 C_2^P = & \int_0^T \frac{\lambda_2(X, Y, Z, T - \tau)}{\omega + \mu_2} \left\{ 1 - \exp \left[-\frac{\omega + \mu_2}{(1 - \beta)R} \tau \right] \right\} d\tau + \frac{\omega}{(\omega + \mu_2)\beta R} \\
 & \times \int_0^\infty \int_{-\infty}^\infty \int_{-\infty}^\infty \int_0^T \left\{ [1 - \mathbf{J}(y, x)] [\lambda_1(\xi, Y - \phi, Z - \Omega, T - \tau) \right. \\
 & + \frac{\omega}{\omega + \mu_2} \lambda_2(\xi, Y - \phi, Z - \Omega, T - \tau)] \exp \left[-\frac{\omega \mu_2 \tau}{(\omega + \mu_2)\beta R} \right] \\
 & \left. - \sqrt{\frac{\beta(T - \tau)}{(1 - \beta)\tau}} \mathbf{H}_1(\tau) \lambda_2(\xi, Y - \phi, Z - \Omega, T - \tau) \right\} \Gamma_1(\phi, \Omega, \tau) G^P(X, \tau) \\
 & \times d\tau d\Omega d\phi d\xi \tag{13b}
 \end{aligned}$$

This solution is written in terms of Goldstein’s \mathbf{J} -function (Goldstein, 1953)

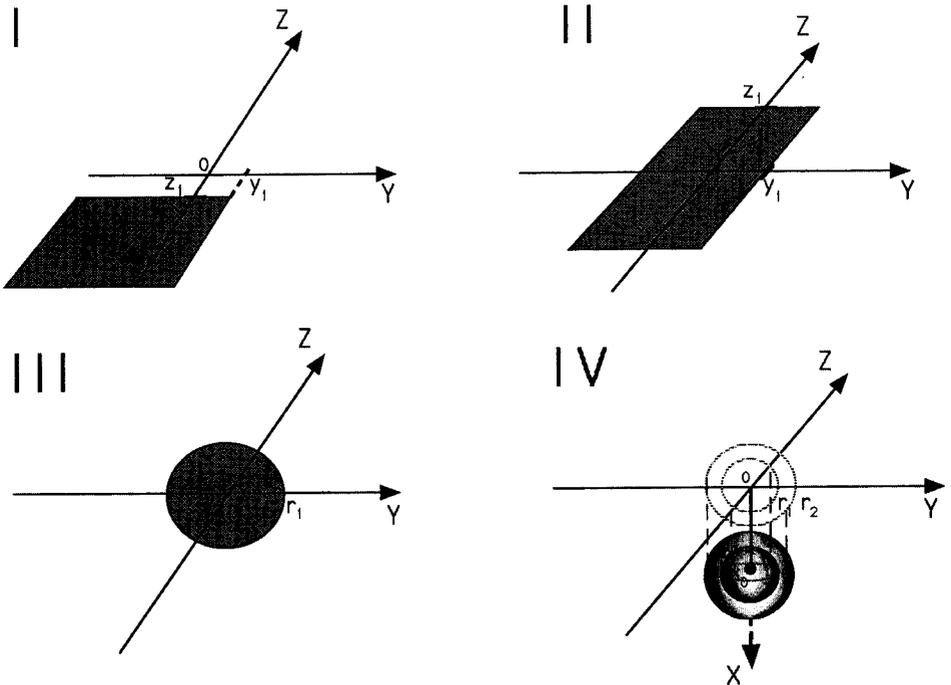


Fig. 1. Transverse geometry for the BVP, IVP and PVP: (I), semi-infinite rectangle ($-\infty < y < y_i$; $-\infty < z < z_i$); (II), finite rectangle ($-y_i < y < y_i - z_i < z < z_i$); (III), circle ($r < r_i$); and (IV), sphere ($0 < r < r_1$, $r_1 < r < r_2$).

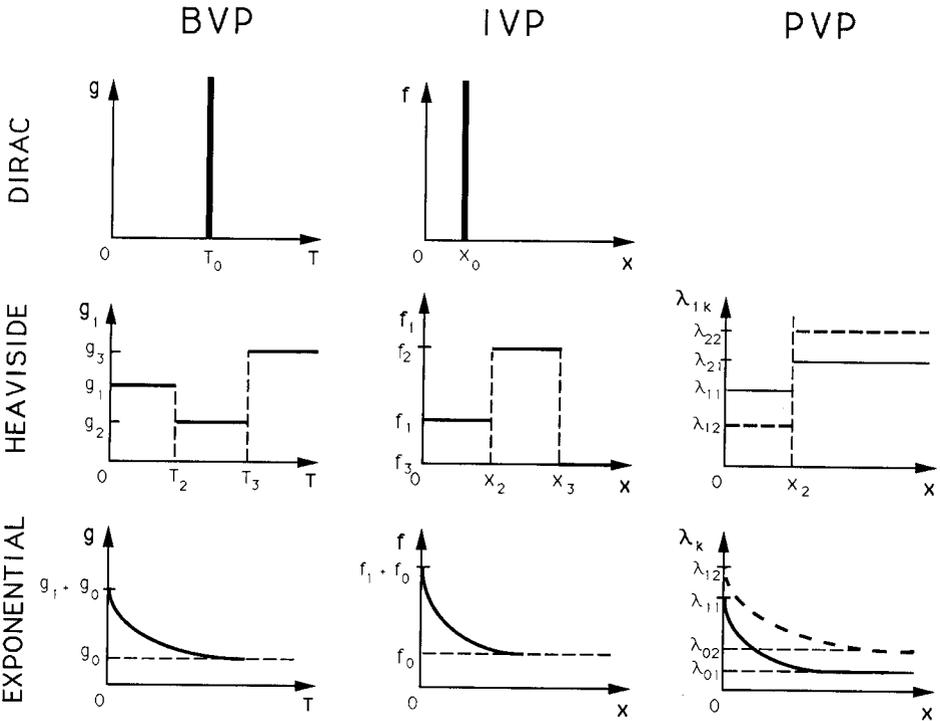


Fig. 2. Schematic of Dirac, Heaviside, and exponential functions to describe the solute input vs. time for the BVP, the initial concentration vs. depth for the IVP, and the production profile for the equilibrium and non-equilibrium phases for the PVP.

$$J(p, q) = 1 - \exp(-q) \int_0^P \exp(-r) I_0[2\sqrt{qr}] dr \tag{14}$$

with

$$p = \frac{\omega^2}{(\omega + \mu_2)\beta R} \tau \quad q = \frac{\omega + \mu_2}{(1 - \beta)R} (T - \tau) \tag{15}$$

Useful properties of the J -function were given by Van Genuchten (1981) and Lassey (1982). The expressions above are solutions to the separate BVP, IVP and PVP. The superposition principle allows ‘combined’ solutions for C_1 and C_2 to be written as the sum of the individual solutions to the BVP, IVP and PVP.

Specific solutions

The previous general solutions, which are admittedly esoteric, provide a

Table 4(a)
Input functions and expressions for the concentration of the BVP

Parameter	Expression
Dirac g & Γ_j	$m\delta(Y - Y_0, Z - Z_0, T - T_0) \& \Gamma_1(Y - Y_0, Z - Z_0, \tau)$
C_1^B	$m \left\{ \exp \left[-\frac{\omega(T - T_0)}{\beta R} \right] \Gamma_1(T - T_0) G^B(X, T - T_0) + \int_0^{T-T_0} \sqrt{\frac{a\tau}{T - T_0 - \tau}} H_1(\tau; T - T_0) \Gamma_1(\tau) G^B(X, \tau) d\tau \right\}$
C_2^B	$\frac{m\omega}{(1 - \beta)R} \int_0^{T-T_0} H_0(\tau; T - T_0) \Gamma_1(\tau) G^B(X, \tau) d\tau$
Heaviside g & Γ_{ij}	$\left\{ \begin{array}{ll} g_i & (i = 1, 2, \dots, n; \quad T_i < T < T_{i+1}) \\ g_0 = 0; T_1 = 0, T_{n+1} \rightarrow \infty & \\ 0 & \text{otherwise} \end{array} \right. \quad \& \quad \text{I} \quad \begin{array}{l} Y < Y_i \quad Z < Z_i \\ \Gamma_2(Y - Y_i, Z - Z_i, \tau) \end{array} \quad \text{II} \quad \begin{array}{l} Y < Y_i \quad Z < Z_i \\ \Gamma_3(Y, Z, \tau; Y_i, Z_i) \end{array} \quad \text{III} \quad \begin{array}{l} \sqrt{Y^2 + Z^2} < r_i \\ \Gamma_4(Y, Z, \tau; r_i) \end{array}$
C_1^B	$\sum_{i=1}^n \int_0^{T-T_i} J(p, q_i) \exp \left[-\frac{\omega\mu_2\tau}{(\omega + \mu_2)\beta R} \right] [g_i \Gamma_{i,j}(\tau) - g_{i-1} \Gamma_{i-1,j}(\tau)] G^B(X, \tau) d\tau$
C_2^B	$\frac{\omega}{\omega + \mu_2} \sum_{i=1}^n \int_0^{T-T_i} [1 - J(q_i, p)] \exp \left[-\frac{\omega\mu_2\tau}{(\omega + \mu_2)\beta R} \right] [g_i \Gamma_{i,j}(\tau) - g_{i-1} \Gamma_{i-1,j}(\tau)] G^B(X, \tau) d\tau$
	with $q_i = \frac{\omega + \mu_2}{(1 - \beta)R} (T - T_i - \tau)$

$$\text{Exponential } g \text{ \& } \Gamma_j \begin{cases} g_0 + g_1 \exp(-\gamma_B T) & T > 0 \\ 0 & \text{otherwise} \end{cases} \quad \& \quad \text{I} \quad \begin{matrix} Y < 0 & Z < 0 \\ \Gamma_2(Y, Z, \tau) \end{matrix} \quad \text{II} \quad \begin{matrix} |Y| < Y_0 & |Z| < Z_0 \\ \Gamma_3(Y, Z, \tau; Y_0, Z_0) \end{matrix} \quad \text{III} \quad \begin{matrix} \sqrt{Y^2 + Z^2} < r_0 \\ \Gamma_4(Y, Z, \tau; r_0) \end{matrix}$$

$$C_1^B \int_0^T \left(g_0 \mathbf{J}(p, q) \exp \left[\frac{\omega \mu_2 \tau}{(\omega + \mu_2) \beta R} \right] + g_1 \exp \left[-\gamma_B (T - \tau) - \frac{\omega \tau}{\beta R} \right] \left\{ \exp \left(-\frac{a\tau}{\gamma_B'} \right) - \Phi_1(\tau) \exp [\gamma_B' (T - \tau)] \right\} \right) \times \Gamma_j(\tau) G^B(X, \tau) d\tau$$

$$C_2^B \int_0^T \left[\frac{\omega g_0}{\omega + \mu_2} [1 - \mathbf{J}(q, p)] \exp \left[-\frac{\omega \mu_2 \tau}{(\omega + \mu_2) \beta R} \right] + \frac{\omega g_1}{(1 - \beta)R} \exp \left[-\frac{\omega \tau}{\beta R} - \frac{\omega + \mu_2}{(1 - \beta)R} (T - \tau) \right] \right. \\ \left. \times \left(\frac{1}{\gamma_B'} \exp \left(-\frac{a\tau}{\gamma_B'} \right) \{1 - \exp [-\gamma_B' (T - \tau)]\} - \Phi_2(\tau) \right) \right] \Gamma_j(\tau) G^B(X, \tau) d\tau$$

$$\{\Phi_1(\tau) = \sum_{n=1}^{\infty} \frac{(a\tau)^n}{n!} \left[\sum_{k=1}^n (-1/\gamma_B')^k \frac{(T - \tau)^{n-k}}{(n - k)!} \right] \Phi_2(\tau) = \sum_{n=1}^{\infty} \frac{(a\tau)^n}{n!} \left[\sum_{k=1}^n (-1/\gamma_B')^k \frac{(T - \tau)^{n-k+1}}{(n - k + 1)(n - k)!} \right] \gamma_B' = \gamma_B - \frac{\omega + \mu_2}{(1 - \beta)R}$$

Table 4(b)
Initial distributions and expressions for the concentration of the IVP

Parameter	Expression
Dirac f & Γ_j	$m\delta(X - X_0, Y - Y_0, Z - Z_0) \& \Gamma_1(Y - Y_0, Z - Z_0, \tau)$
C_1^I	$m \exp\left(-\frac{\omega T}{\beta R}\right) \Gamma_1(T) G^I(X_0, T) + m \int_0^T \left[\frac{\omega}{\beta R} H_0(\tau; T) + \sqrt{a\tau/(T-\tau)} H_1(\tau; T) \right] \Gamma_1(\tau) G^I(X_0, \tau) d\tau$
C_2^I	$\frac{m\omega}{(1-\beta)R} \int_0^T \left[H_0(\tau; T) + \frac{\omega}{\beta R} \sqrt{\frac{T-\tau}{a\tau}} H_1(\tau; T) \right] \Gamma_1(\tau) G^I(X_0, \tau) d\tau$
Heaviside f & $\Gamma_{i,j}(\tau)$	$\left\{ \begin{array}{l} f_i \quad \begin{array}{l} X_i < X < X_{i+1} \\ (i = 1, 2, \dots, n; \\ f_0 = 0; X_1 = 0, X_{n+1} \rightarrow \infty) \end{array} \\ 0 \quad \text{otherwise} \end{array} \right. \quad \& \quad \text{I} \quad \begin{array}{l} Y < Y_i \quad Z < Z_i \\ \Gamma_2(Y - Y_i, Z - Z_i, \tau) \end{array} \quad \text{II} \quad \begin{array}{l} Y < Y_i \quad Z < Z_i \\ \Gamma_3(Y, Z, \tau; Y_i, Z_i) \end{array} \quad \text{III} \quad \begin{array}{l} \sqrt{Y^2 + Z^2} < r_i \\ \Gamma_4(Y, Z, \tau; r_i) \end{array}$ $\left\{ \begin{array}{l} f_i \quad \begin{array}{l} r_{i-1} < r < r_i \\ (i = 1, 2, \dots, n; f_{n+1} = 0; r_0 = 0) \end{array} \\ 0 \quad \text{otherwise} \end{array} \right. \quad \& \quad \text{IV} \quad \begin{array}{l} r = \sqrt{(X - X_0)^2 + Y^2 + Z^2} \\ \Gamma_5(\xi, Y, Z, \tau; X_0, r_i) \end{array}$

I, II, III	$\sum_{i=1}^n \left\{ \exp\left(-\frac{\omega T}{\beta R}\right) [f_i \Gamma_{i,j}(T) - f_{i-1} \Gamma_{i-1,j}(T)] G_1^I(X, T; X_i) \right.$																					
C_1^I	$\left. + \int_0^T \left[\frac{\omega}{\beta R} H_0(\tau; T) + \sqrt{a\tau/(T-\tau)} H_1(\tau; T) \right] [f_i \Gamma_{i,j}(\tau) - f_{i-1} \Gamma_{i-1,j}(\tau)] G_1^I(X, \tau; X_i) d\tau \right\}$																					
IV	$\sum_{i=1}^n \left\{ \exp\left(-\frac{\omega T}{\beta R}\right) (f_i - f_{i-1}) \Gamma_{i-1,5}(T) + \int_0^T \left[\frac{\omega}{\beta R} H_0(\tau; T) + \sqrt{a\tau/(T-\tau)} H_1(\tau; T) \right] (f_i - f_{i-1}) \Gamma_{i-1,5}(\tau) d\tau \right\}$																					
I, II, III	$f(X, Y, Z) \exp\left[-\frac{\omega + \mu_2}{(1-\beta)R} T\right] + \frac{\omega}{(1-\beta)R}$																					
C_2^I	$\times \sum_{i=1}^n \left\{ \int_0^T \left[H_0(\tau; T) + \frac{\omega}{\beta R} \sqrt{\frac{T-\tau}{a\tau}} H_1(\tau; T) \right] [f_i \Gamma_{i,j}(\tau) - f_{i-1} \Gamma_{i-1,j}(\tau)] G_1^I(X, \tau; X_i) d\tau \right\}$																					
IV	$f(X, Y, Z) \exp\left[-\frac{\omega + \mu_2}{(1-\beta)R} T\right] + \frac{\omega}{(1-\beta)R} \sum_{i=1}^n \int_0^T \left[H_0(\tau; T) + \frac{\omega}{\beta R} \sqrt{\frac{T-\tau}{a\tau}} H_1(\tau; T) \right] (f_i - f_{i+1}) \Gamma_{i-1,5}(\tau) d\tau$																					
Exponential f & Γ_j	<table style="width: 100%; border: none;"> <tr> <td style="border-left: 1px solid black; padding-left: 10px;"> $f_0 + f_1 \exp(-\gamma_1 X) \quad X > 0$ </td> <td style="padding: 0 10px;">& I</td> <td style="padding: 0 10px;">$Y < 0 \quad Z < 0$</td> <td style="padding: 0 10px;">II</td> <td style="padding: 0 10px;">$Y < Y_0 \quad Z < Z_0$</td> <td style="padding: 0 10px;">III</td> <td style="padding: 0 10px;">$\sqrt{Y^2 + Z^2} < r_0$</td> </tr> <tr> <td style="border-left: 1px solid black; padding-left: 10px;">0</td> <td colspan="6" style="padding-left: 10px;">otherwise</td> </tr> <tr> <td style="border-left: 1px solid black;"></td> <td></td> <td style="padding: 0 10px;">$\Gamma_2(Y, Z, \tau)$</td> <td></td> <td style="padding: 0 10px;">$\Gamma_3(Y, Z, \tau; Y_0, Z_0)$</td> <td></td> <td style="padding: 0 10px;">$\Gamma_4(Y, Z, \tau; r_0)$</td> </tr> </table>	$f_0 + f_1 \exp(-\gamma_1 X) \quad X > 0$	& I	$Y < 0 \quad Z < 0$	II	$ Y < Y_0 \quad Z < Z_0$	III	$\sqrt{Y^2 + Z^2} < r_0$	0	otherwise								$\Gamma_2(Y, Z, \tau)$		$\Gamma_3(Y, Z, \tau; Y_0, Z_0)$		$\Gamma_4(Y, Z, \tau; r_0)$
$f_0 + f_1 \exp(-\gamma_1 X) \quad X > 0$	& I	$Y < 0 \quad Z < 0$	II	$ Y < Y_0 \quad Z < Z_0$	III	$\sqrt{Y^2 + Z^2} < r_0$																
0	otherwise																					
		$\Gamma_2(Y, Z, \tau)$		$\Gamma_3(Y, Z, \tau; Y_0, Z_0)$		$\Gamma_4(Y, Z, \tau; r_0)$																

Table 4(b) (Continued)

Parameter	Expression
C_1^1	$\exp\left(-\frac{\omega T}{\beta R}\right) \Gamma_j(T) [f_0 G_1^1(X, T; 0) + f_1 G_2^1(X, T; \gamma_1)]$ $+ \int_0^T \left[\frac{\omega}{\beta R} H_0(\tau; T) + \sqrt{a\tau/(T-\tau)} H_1(\tau; T) \right] \Gamma_j(\tau) [f_0 G_1^1(X, \tau; 0) + f_1 G_2^1(X, \tau; \gamma_1)] d\tau$
C_2^1	$f(X, Y, Z) \exp\left(-\frac{\omega + \mu_2}{\beta R} T\right) + \frac{\omega}{(1-\beta)R} \int_0^T \left[H_0(\tau; T) + \frac{\omega}{\beta R} \sqrt{\frac{T-\tau}{a\tau}} H_1(\tau; T) \right]$ $\times \Gamma_j(\tau) [f_0 G_1^1(X, \tau; 0) + f_1 G_2^1(X, \tau; \gamma_1)] d\tau$

Table 4(c)
Production profile and expressions for the concentration of the PVP

Parameter	Expression
Heaviside λ_k & $\Gamma_{ij}(\tau)$	$\left\{ \begin{array}{ll} \lambda_{i,k} & \begin{array}{l} X_i < X < X_{i+1} \\ (i = 1, 2, \dots, n; k = 1, 2; \\ \lambda_{0,k} = 0; X_1 = 0; X_{n+1} \rightarrow \infty) \end{array} & \text{\& I} & \begin{array}{l} Y < Y_i \quad Z < Z_i \\ \Gamma_2(Y - Y_i, Z - Z_i, \tau) \end{array} & \text{\Sigma II} & \begin{array}{l} Y < Y_i \quad Z < Z_i \\ \Gamma_3(Y, Z, \tau; Y_i, Z_i) \end{array} & \text{\textcircled{III}} & \begin{array}{l} \sqrt{Y^2 + Z^2} < r_i \\ \Gamma_4(Y, Z, \tau; r_i) \end{array} \\ \\ 0 & \text{otherwise} \end{array} \right.$
	$\left\{ \begin{array}{ll} \lambda_{i,k} & \begin{array}{l} r_{i-1} < r < r_i \\ (i = 1, 2, \dots, n; \\ k = 1, 2; \lambda_{n+1,k} = 0; r_0 = 0) \end{array} & \text{\& IV} & \begin{array}{l} r = \sqrt{(X - X_0)^2 + Y^2 + Z^2} \\ \Gamma_5(\xi, Y, Z, \tau; X_0, r_i) \end{array} \\ \\ 0 & \text{otherwise} \end{array} \right.$
I, II, III	$\frac{1}{\beta R} \sum_{i=1}^n \int_0^T \{ [\lambda_{i,1} \Gamma_{i,j}(\tau) - \lambda_{i-1,1} \Gamma_{i-1,j}(\tau)] \mathbf{J}(q, p)$
C_1^P	$+ \frac{\omega}{\omega + \mu_2} [\lambda_{i,2} \Gamma_{i,j}(\tau) - \lambda_{i-1,2} \Gamma_{i-1,j}(\tau)] [1 - \mathbf{J}(q, p)] \} \exp \left[-\frac{\omega \mu_2 \tau}{(\omega + \mu_2) \beta R} \right] G_1^P(X, \tau; X_i) d\tau$
IV	$\frac{1}{\beta R} \sum_{i=1}^n \int_0^T \{ (\lambda_{i,1} - \lambda_{i+1,1}) \mathbf{J}(p, q) + \frac{\omega}{\omega + \mu_2} (\lambda_{i,2} - \lambda_{i+1,2}) [1 - \mathbf{J}(q, p)] \} \Gamma_{i,j}(\tau) \exp \left[-\frac{\mu_1 \tau}{\beta R} - \frac{\omega \mu_2 \tau}{(\omega + \mu_2) \beta R} \right] d\tau$

Table 4(c) (Continued)

Parameter	Expression
I, II, III	$\frac{\lambda_2(X, Y, Z)}{\omega + \mu_2} \left\{ 1 - \exp \left[-\frac{\omega + \mu_2}{(1 - \beta)R} T \right] \right\} + \frac{\omega}{(\omega + \mu_2)\beta R} \sum_{i=1}^n \int_0^T \left(\{ \lambda_{i,1} \Gamma_{i,j}(\tau) - \lambda_{i-1,1} \Gamma_{i-1,j}(\tau) + \frac{\omega}{\omega + \mu_2} [\lambda_{i,2} \Gamma_{i,j}(\tau) \right.$
C ₂ ^P	$\left. - \lambda_{i-1,2} \Gamma_{i-1,j}(\tau) \} [1 - \mathbf{J}(q, p)] \exp \left[-\frac{\omega \mu_2 \tau}{(\omega + \mu_2)\beta R} \right] - [\lambda_{i,2} \Gamma_{i,j}(\tau) - \lambda_{i-1,2} \Gamma_{i-1,j}(\tau)] \sqrt{\frac{\beta(T - \tau)}{(1 - \beta)\tau}} H_1(\tau; T) \right) G_1^P(X, \tau; X_i) d\tau$
IV	$\frac{\lambda_2(X, Y, Z)}{\omega + \mu_2} \left\{ 1 - \exp \left[-\frac{\omega + \mu_2}{(1 - \beta)R} T \right] \right\} + \frac{\omega}{(\omega + \mu_2)\beta R} \sum_{i=1}^n \int_0^T \left\{ [\lambda_{i,1} - \lambda_{i+1,1} + \frac{\omega}{\omega + \mu_2} (\lambda_{i,2} - \lambda_{i+1,2})] \right.$
	$\left. \times [1 - \mathbf{J}(q, p)] \exp \left[-\frac{\omega \mu_2 \tau}{(\omega + \mu_2)\beta R} \right] - (\lambda_{i,2} - \lambda_{i+1,2}) \sqrt{\frac{\beta(T - \tau)}{(1 - \beta)\tau}} H_1(\tau; T) \right\} \exp \left(-\frac{\mu_1 \tau}{\beta R} \right) \Gamma_{i,j}(\tau) d\tau$
Exponential λ_k & Γ_j	$\begin{cases} \lambda_{0,k} + \lambda_{1,k} \exp(-\gamma_{k,p} X) & \text{I} & Y < 0 \quad Z < 0 & \text{II} & Y < Y_0 \quad Z < Z_0 & \text{III} & \sqrt{Y^2 + Z^2} < r_0 \\ (k = 1, 2) X > 0 & & \Gamma_2(Y, Z, \tau) & & \Gamma_3(Y, Z, \tau; Y_0, Z_0) & & \Gamma_4(Y, Z, \tau; r_0) \\ 0 & \text{otherwise} & & & & & \end{cases}$
C ₁ ^P	$\int_0^T \{ [\lambda_{0,1} G_1^P(X, \tau; 0) + \lambda_{1,1} G_2^P(X, \tau; \lambda_{1,p})] \mathbf{J}(p, q) + \frac{\omega}{\omega + \mu_2} [\lambda_{0,2} G_1^P(X, \tau; 0) + \lambda_{1,2} G_2^P(X, \tau; \gamma_{2,p})] [1 - \mathbf{J}(q, p)] \} \exp \left[-\frac{\omega \mu_2 \tau}{(\omega + \mu_2)\beta R} \right] \Gamma_j(\tau) d\tau$

$$\begin{aligned}
 C_2^P &= \frac{\lambda_2(X, Y, Z)}{\omega + \mu_2} \left\{ 1 - \exp \left[-\frac{\omega + \mu_2}{(1 - \beta)R} T \right] \right\} + \frac{\omega}{(\omega + \mu_2)\beta R} \int_0^T \left(\{\lambda_{0,1} G_1^P(X, \tau; 0) + \lambda_{1,1} G_2^P(X, \tau; \gamma_{1,p})\} \right. \\
 &+ \frac{\omega}{\omega + \mu_2} [\lambda_{0,2} G_1^P(X, \tau; 0) + \lambda_{1,2} G_2^P(X, \tau; \lambda_{2,p})] [1 - J(q, p)] \exp \left[-\frac{\omega \mu_2 \tau}{(\omega + \mu_2)\beta R} \right] \\
 &\left. - [\lambda_{0,2} G_1^P(X, \tau; 0) + \lambda_{1,2} G_2^P(X, \tau; \gamma_{2,p})] \sqrt{\frac{\beta(T - \tau)}{(1 - \beta)\tau}} H_1(\tau; T) \right) \Gamma_j(\tau) d\tau
 \end{aligned}$$

useful foundation for deriving specific analytical solutions applicable to simple boundary, initial, or production conditions. We derived solutions for the BVP and IVP assuming a Dirac distribution, and for the BVP, IVP, or PVP assuming Heaviside or exponential distributions in (1) semi-infinite rectangular, (2) finite rectangular, (3) cylindrical, and (4) spherical regions. All solutions are based on Fourier transforms and a Cartesian coordinate system.

The different areas where solute is applied (BVP), initially distributed (IVP), or produced (PVP), are sketched in Fig. 1. The first three cases are in the transverse plane while the spherical case, which pertains only to the IVP and PVP, includes the longitudinal coordinate. The magnitude for g needs to be specified as a function of time for the BVP while for the IVP and λ for the PVP should be given as a function of the longitudinal distance for cases I, II and III, or the radial distance for case IV. The input functions for the BVP, the initial concentrations for the PVP, and the λ profile for the PVP are given schematically in Fig. 2. We continue by presenting the solutions for the various cases of the BVP, IVP and PVP, along with some brief comments regarding the method of solution.

Table 4(a) lists solutions for the BVP, and specifications of the input functions and the type of transverse auxiliary function on which they are based. The derivation of these transverse functions, I' , is fairly straightforward; the specific independent variables for each problem are listed in the left-hand column of Table 4(a). The entire solution can be obtained by inserting the auxiliary functions given in Tables 2 and 3. For the Dirac input, i.e. for the case where a solute mass m is applied instantaneously at position (Y_0, Z_0) at the surface at time T_0 , the expression for C_1 can be readily derived from the general solution. The solution for C_2 was obtained with the help of Fubini's theorem. In the case of a Heaviside-type input, an arbitrary number of solute pulses with different constant concentrations is applied. The problem was first cast in terms of the J-function, after which the expressions could be simplified by changing the order of integration and integration by parts using some of the properties of the J-function listed in appendix A of Van Genuchten (1981). The integration with respect to the transverse coordinates, Y and Z , was based on elementary properties of the error function (Gautschi, 1965). Case I concerns solute application to a semi-infinite rectangular area; its finite corner position (Y_i, Z_i) may vary for each pulse. Similarly, cases II and III involve solute application to finite rectangular and circular areas.

The third input function consists of a term which decreases exponentially with time, as specified in Table 4(a). The solute in this case is applied to the same region as for the Heaviside input function; however, the transverse dimensions are time invariant. Evaluation of the general solution containing

g_0 is very similar as for the Heaviside input. Evaluation of the g_1 function with exponential decrease was done by applying Fubini's theorem and partial integration. The resulting expression consisted of the product of an exponential function and the zero-order modified Bessel function. Since no expression for this integral appears to be available (cf. Luke, 1962), the series representation 9.6.12 of Olver (1965)

$$I_0[\sqrt{a\tau\eta}] = 1 + \frac{a\eta}{(1!)^2}\tau + \frac{(a\eta)^2}{(2!!)^2}\tau^2 + \frac{(a\eta)^3}{(3!)^2}\tau^3 + \dots \tag{16}$$

was used to integrate (2.321.2) of Gradshteyn and Ryzhik (1980). This procedure led to

$$\int_{\eta}^T \exp(\gamma_B'\tau) I_0[2\sqrt{a(\tau-\eta)\eta}] d\tau = \frac{1}{\gamma_B'} \exp(\gamma_B'T) \left\{ I_0[2\sqrt{a(T-\eta)\eta}] + \Phi(\eta) \right\} - \frac{1}{\gamma_B'} \exp\left[\left(\gamma_B' - \frac{a}{\gamma_B'}\right)\eta\right] \tag{17a}$$

$$\Phi(\eta) = \sum_{n=1}^{\infty} \frac{(a\eta)^n}{n!} \left(\sum_{k=1}^n \frac{(-1)^k (T-\eta)^{n-k}}{\gamma_B'^k (n-k)!} \right) \text{ and } \gamma_B' = \gamma_B - \frac{\omega + \mu_2}{(1-\beta)R} \tag{17b}$$

In most cases a convergent solution was obtained for a maximum n value of 25; however, the solution was less accurate for, among other factors, relatively large values for a and T . Similar problems occur for the series approximation of the J-function by De Smedt and Wierenga (1979b) (cf. Lassey, 1982).

Table 4(b) contains the different types of initial conditions for which the IVP was solved, along with the definitions of variables in the auxiliary transverse function, and the semi-infinite and finite rectangular, cylindrical and spherical regions. For the Dirac initial condition, i.e. for an instantaneous release of a solute mass m at (X_0, Y_0, Z_0) , the IVP can be readily solved. Note that evaluation of the term containing f in C_2^I is impractical for the Dirac condition. Specific solutions for the Heaviside-type initial distribution, consisting of n semi-infinite or finite parallelepipeds, cylinders, or spherical shells, were obtained through integration with respect to the longitudinal and transverse coordinates. The identity

$$\int_{X_i}^{X_{i+1}} G^I(X, \tau) d\xi = G_1^I(X, \tau; \xi) \Big|_{X_{i+1}}^{X_i} \tag{18}$$

could be established with properties of the error function and the Laplace transform; the expression for G_1^I was included in Table 2. The solution for C_2^I again involved the application of Fubini's theorem to evaluate one of the

integrals with respect to time. For the spherical IVP, where the solute concentration is uniformly distributed in shells, the evaluation of the integrals was hampered by the presence of variable integration limits. For the exponentially decaying distribution with depth ($0 < X < \infty$), the integration with respect to the transverse coordinates was the same as for the Heaviside distribution with an arbitrary number of steps. Integration in the longitudinal direction was based on Eq. (18) and

$$\int_0^{\infty} \exp(-\gamma_1 \xi) G^I(X, \tau) d\xi = G_2^I(X, \tau) \quad (19)$$

which was derived through integration by parts and using properties of the error function and expression (3.322.2) of Gradshteyn and Ryzhik (1980). This approach is an alternative to evaluating integrals using Laplace transforms. Note that the IVP was not solved for an initial profile that decreases exponentially from the center of a spherical region.

Finally, several specific solutions were obtained for the PVP assuming only a spatial dependency of λ_k . Time dependency can easily be introduced (cf. Lindstrom and Boersma, 1989), although it is then quite difficult to simplify the general solution significantly. Table 4(c) contains the production functions and the expressions for the concentrations and auxiliary functions, Γ_j , for seven problems. The λ_k profiles were described with Heaviside and exponential functions for the same geometries as the PVP. The methodology to obtain the specific solutions is similar as used previously for the BVP and the IVP.

All integrals in the analytical solutions of Table 4 were evaluated with Gauss-Chebyshev quadrature (Carnahan et al., 1969). This method allows greater flexibility in the number of integration points, as opposed to, for example, Gaussian integration. A disadvantage, particularly for the solutions involving multiple integration, is the increased amount of computer time. If this is of major concern, one may prefer to solve the entire problem numerically. Further information regarding the computer program to evaluate the solutions in Table 4 can be obtained from the senior author.

Examples

In this section we provide several illustrations of results obtained with the analytical solutions from Table 4. Since the three-dimensional non-equilibrium model is based on existing and generally well-known one-dimensional non-equilibrium and three-dimensional equilibrium models, we will not focus on the conceptual aspects of the predicted concentration profiles, nor will we provide a complete overview of results for all different cases. For example, Dirac functions, spherical geometries, and flux-averaged concentrations will

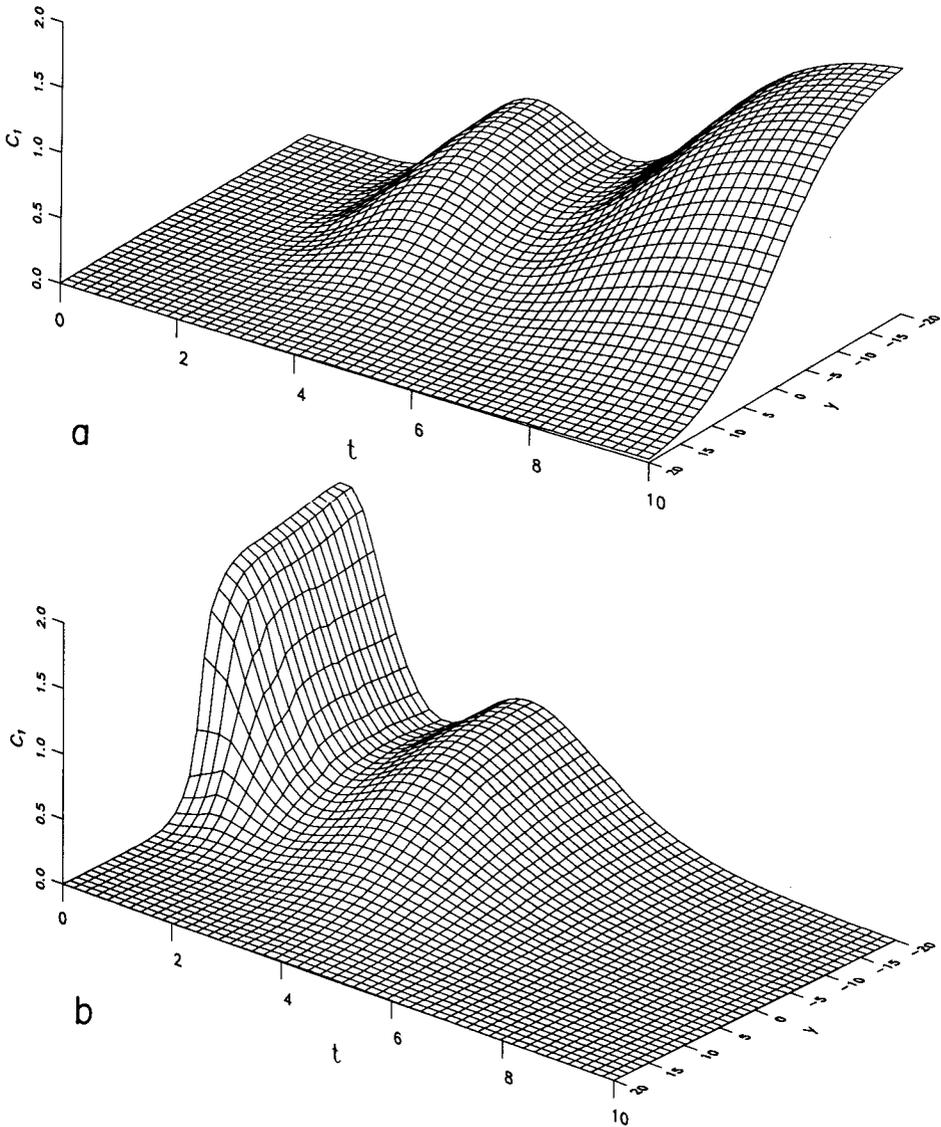


Fig. 3. Breakthrough curve at $x = L = 40$, $z = -20$, and $-20 < y < 20$ for a Heaviside function and a semi-infinite rectangular geometry ($-\infty < y < 0$, $-\infty < z < 0$) with $v = 10$, $R = c_0 = 1$, $D_x = 20$, $D_y = D_z = 10$, $\mu_1 = \mu_2 = 0$, $\omega = 5$, $\beta = 0.9$: (a) BVP with $(g_1, g_2, g_3) = (5, 0, 2)$ and $(t_1, t_2, t_3) = (0, 0.5, 3)$; and (b) IVP with $(f_1, f_2, f_3) = (5, 0, 2)$ and $(x_1, x_2, x_3) = (0, 5, 30)$.

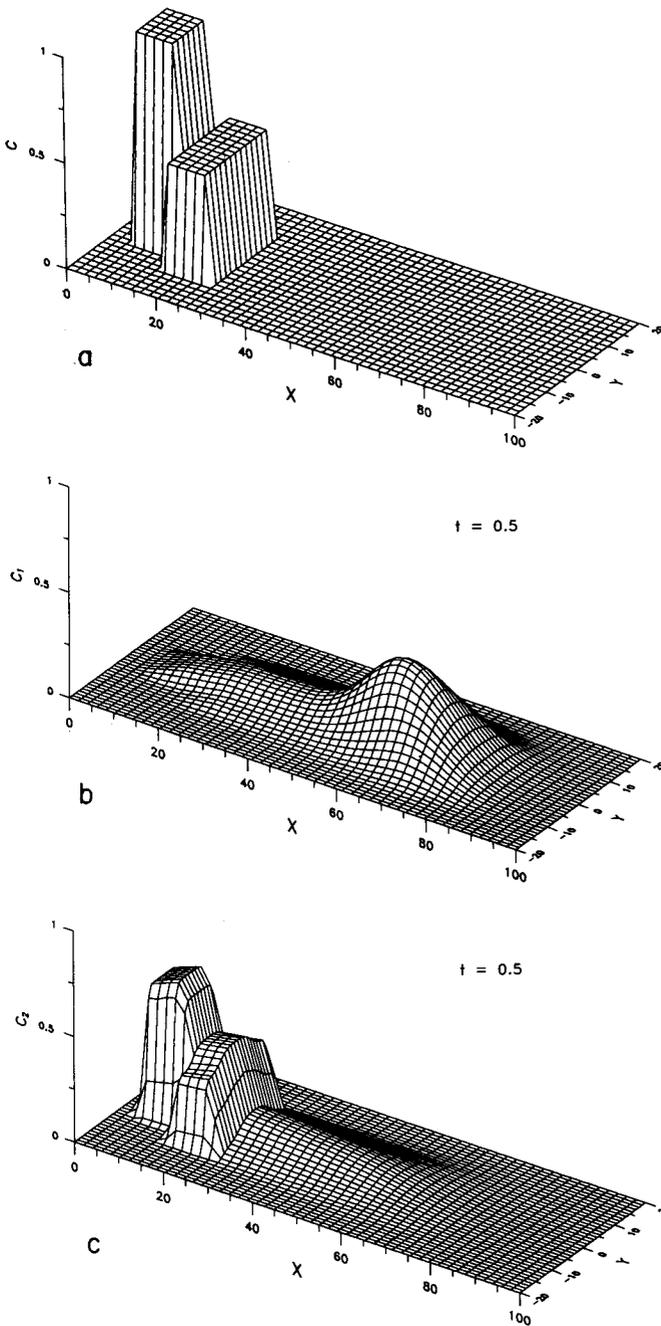


Fig. 4.

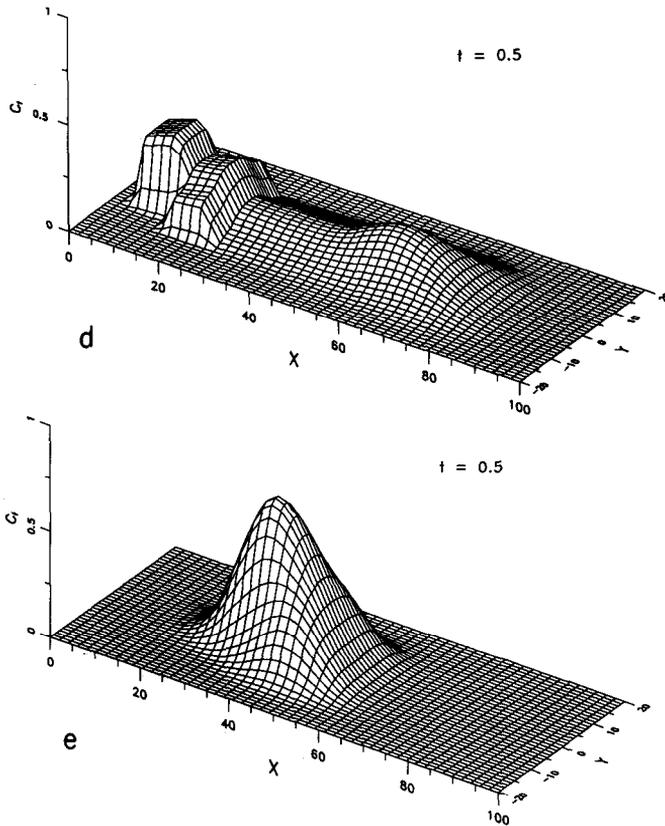


Fig. 4. IVP involving a Heaviside profile of finite rectangular regions with $v = 50$, $R = c_0 = 1$, $D_x = 20$, $D_y = D_z = 5$, $\mu_1 = \mu_2 = 0$, and $L = 100$. Two-dimensional solute profiles at $z = 0$: (a) initial distribution for $C_1 = C_2$ with $(f_1, f_2, f_3, f_4) = (0, 1, 0.5, 0)$, $(x_1, x_2, x_3, x_4) = (0, 5, 10, 15)$, $(y_2, y_3) = (z_2, z_3) = (5, 10)$; (b) C_1 profile at $t = 0.5$ for $\beta = 0.5$ and $\omega = 1$; (c) C_2 profile at $t = 0.5$ for $\beta = 0.5$ and $\omega = 1$; (d) C_T profile at $t = 0.5$ for $\beta = 0.5$ and $\omega = 1$; (e) C_T profile at $t = 0.5$ for $\beta = 0.9$ and $\omega = 5$.

not be treated. The model parameters are dimensional in all examples given here, except for μ, λ and ω ; no units will be specified for these rate parameters, and hence the results can be interpreted using any dimensionally consistent set of parameters. The dimensionless concentration is investigated as a function of dimensional time and position.

The first example involves breakthrough curves stemming from a result of a Heaviside step input or initial condition for a semi-infinite transverse region. Figure 3(a) presents the equilibrium resident concentration for the BVP as a function of t and y for pulse and step input, with intermediate application of solute-free water, at the surface region given by $y < 0$ and $z < 0$. During transport through the soil the magnitude of the first solute peak, $g_1 = 5$,

has been reduced considerably at the soil outlet. Notice that a steady-state concentration equal to $g_2 = 2$ is established for $t > 3$. Figure 3(b) shows the breakthrough curve for the IVP with a similar initial profile as the input function for the BVP in Fig. 3(a). The solute peaks are somewhat higher and a clear dip between solute peaks can be distinguished at about $t = 1$, in contrast to the BVP. The transverse solute profiles for both cases are fairly symmetrical about $y = 0$.

The second example involves solute distributions in the xy -plane at $t = 0.5$ and $z = 0$ resulting from a uniform initial solute distribution in the form of two parallelepipeds. The initial distribution is sketched in Fig. 4(a). The two-dimensional profiles for C_1 , C_2 , and C_T are sketched in Figs. 4(b), (c) and (d), respectively, using $\beta = 0.5$ and $w = 1$. The concentration in the equilibrium phase is largely determined by advection and dispersion; the initially distinct solute peaks have disappeared as a result of dispersion (Fig. 4(b)). Because no advective or dispersive transport can occur in phase 2, the C_2 profile still resembles the initial profile at $t = 0.5$. The solute in the region $x > 25$, i.e. near the toe of the C_2 profile, arrived there by movement in phase 1 and transfer between the two phases according to Eq. (3b). Exchange between the two phases also causes a tail to develop in the equilibrium profile (Fig. 4b). The resulting total concentration, C_T , is plotted in Fig. 4(d). A similar C_T profile for the 'equilibrium' condition ($\beta = 0.9$, $w = 5$) is provided in Fig. 4(e). Notice that the non-equilibrium profile is contained within a smaller region of the soil and with higher maximum concentrations.

A third example is used to illustrate the effects of changes in the first-order decay term, μ . Figure 5(a) shows how the solute is initially distributed between depths $x = 5$ and 15 in two parallelepipedal areas. The solute will move downward as a result of the application of solute-free water at the surface. Consider a hypothetical case where, for instance through bioremediation, one hopes to decrease the concentration to sufficiently low levels before the solute reaches an underlying aquifer. Figures 5(b)-(d) show the contours of the total concentration, C_T , in the xy -plane at $t = 1$ for an increasing μ assuming equal decay in the equilibrium and non-equilibrium phases. This rather simplistic example clearly demonstrates decreasing solute concentrations in both directions as a result of decay. Because dispersion and diffusion are relatively important compared with advection, part of the solute moves upward from the initial area toward the soil surface.

Fig. 5. (opposite) IVP involving a Heaviside profile of finite rectangular regions with $v = 5$, $\mathbf{R} = c_0 = 1$, $D_x = 40$, $D_y = D_z = 10$, $\mu_1 = \mu_2 = 0$, $\omega = 5$, $\beta = 0.9$. (a) Initial distribution with $(f_1, f_2, f_3, f_4) = (0, 2, 1, 0)$, $(x_1, x_2, x_3, x_4) = (0, 5, 10, 15)$, $(y_2, y_3) = (5, 2.5)$, and $(z_2, z_3) = (5, 2.5)$; (b) C_T contours at $z = 0$ for $\mu_1 = \mu_2 = 0$; (c) C_T contours at $z = 0$ for $\mu_1 = \mu_2 = 0.5$; (d) C_T contours at $z = 0$ for $\mu_1 = \mu_2 = 1.0$.

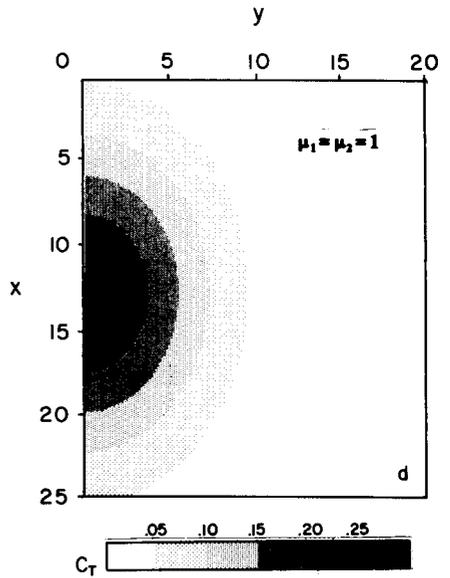
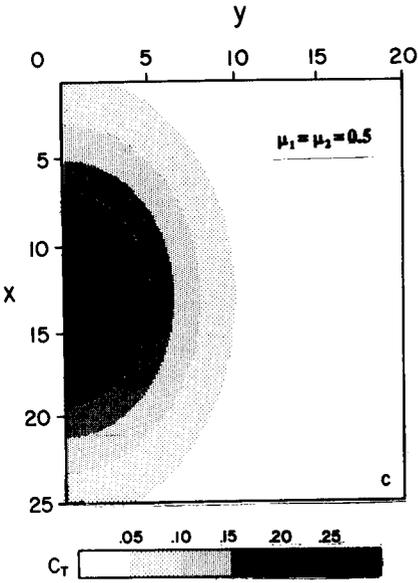
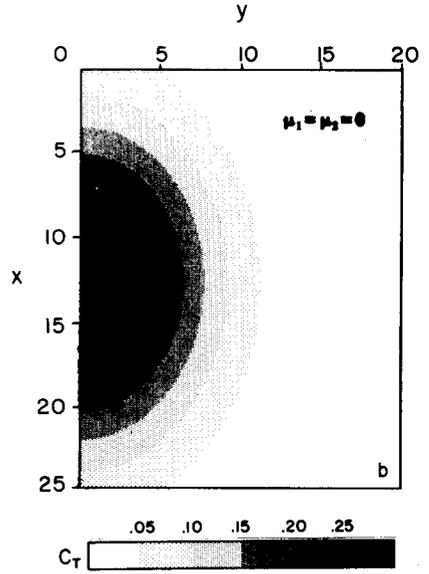
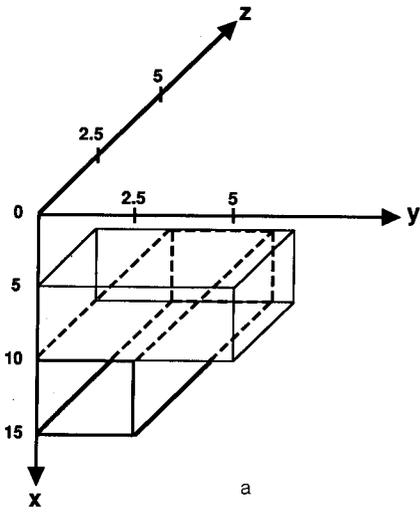


Fig. 5.

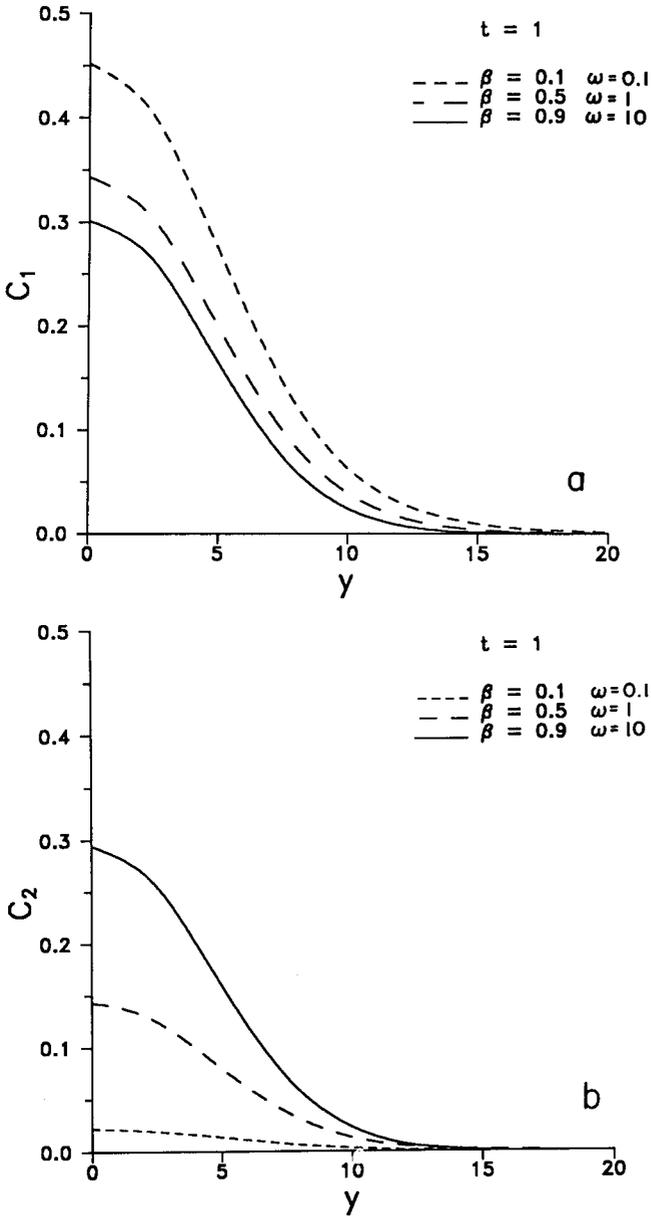


Fig. 6. Transverse solute profile at $x = 10$, $z = 0$ for a BVP and a step input ($g = 1$ for $t > 0$) to a circular area of the surface ($r < 5$) with $\nu = 10$, $R = c_0 = 1$, $D_x = 20$, $D_y = D_z = 10$, $\mu_1 = \mu_2 = 0$, and $L = 20$ for various non-equilibrium conditions: (a) $C_1(y)$ profile at $t = 1$; (b) $C_2(y)$ profile at $t = 1$; (c) $C_1(y)$ profile at $t = 5$; (d) $C_2(y)$ profile at $t = 5$.

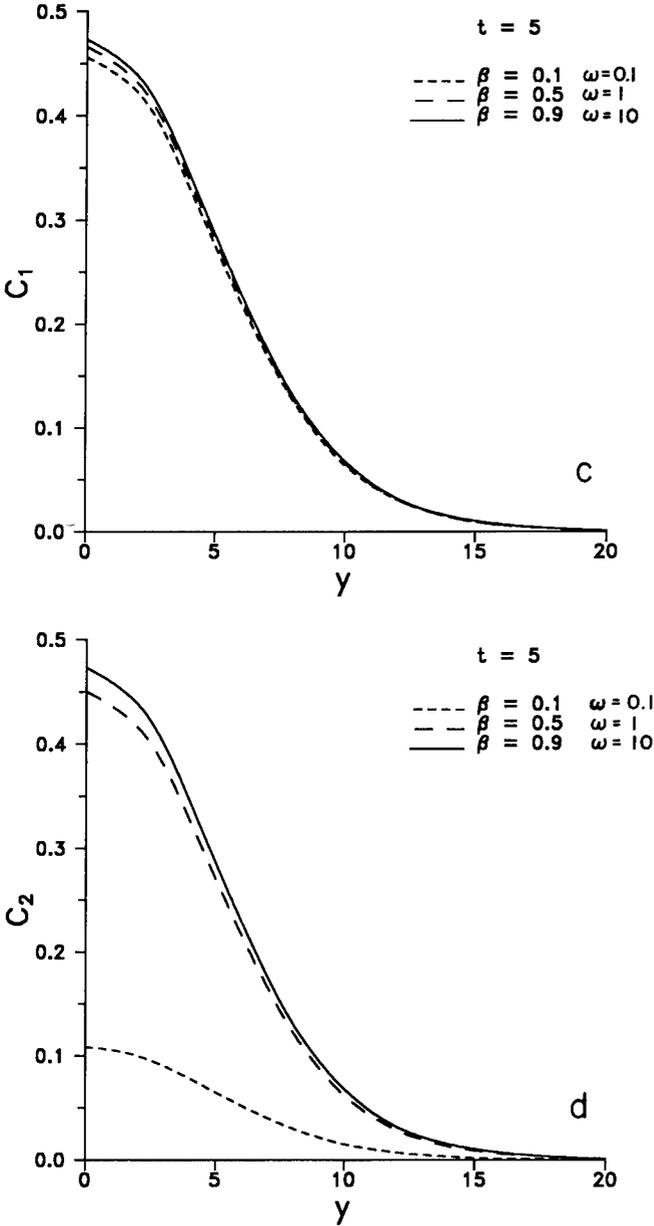


Fig. 6. (Continued).

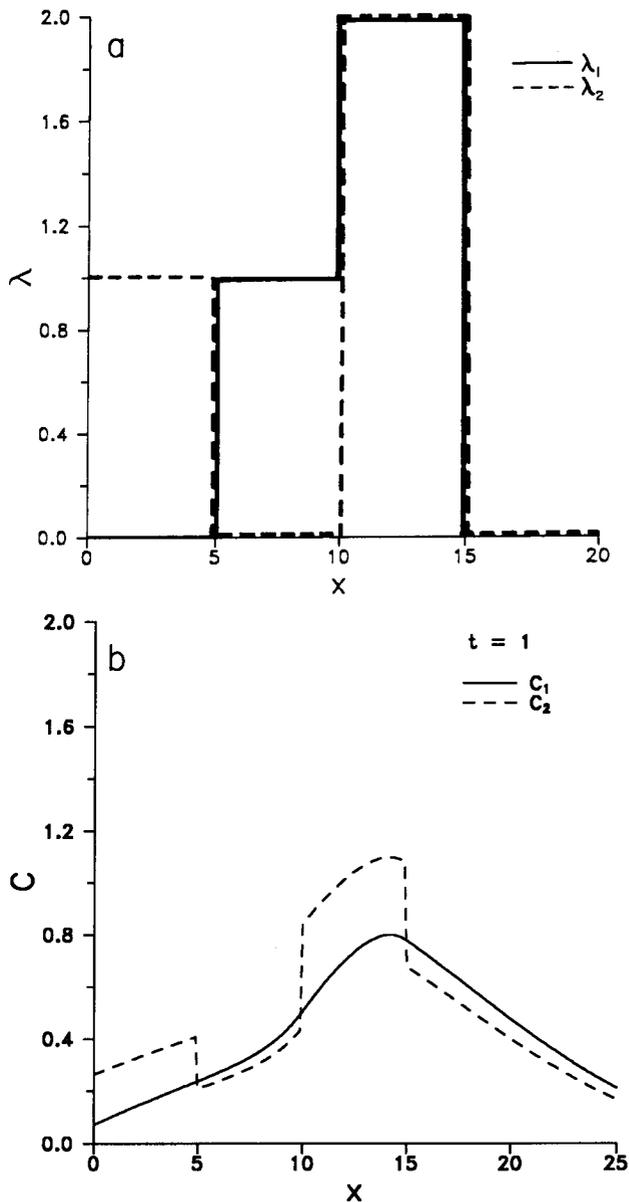


Fig. 7. PVP involving a Heaviside production profile for a semi-infinite rectangular region ($-\infty < y < 0$ and $-\infty < z < 0$) at $y = z = -10$ with $v = 10$, $R = c_0 = 1$, $D_x = 20$, $D_y = D_z = 10$, $\mu_1 = \mu_2 = 0$, $\omega = 5$, $\beta = 0.9$, and $L = 25$: (a) production profiles $\lambda_1(x)$, $(\lambda_{11}, \lambda_{21}, \lambda_{31}, \lambda_{41}) = (0, 1, 2, 0)$ and $\lambda_2(x)$, $(\lambda_{12}, \lambda_{22}, \lambda_{32}, \lambda_{42}) = (1, 0, 2, 0)$, with $(x_1, x_2, x_3, x_4) = (0, 5, 10, 15)$; (b) concentration profiles $C_1(x)$ and $C_2(x)$ at $t = 1$; (c) concentration profiles $C_1(x)$ and $C_2(x)$ at $t = 10$.

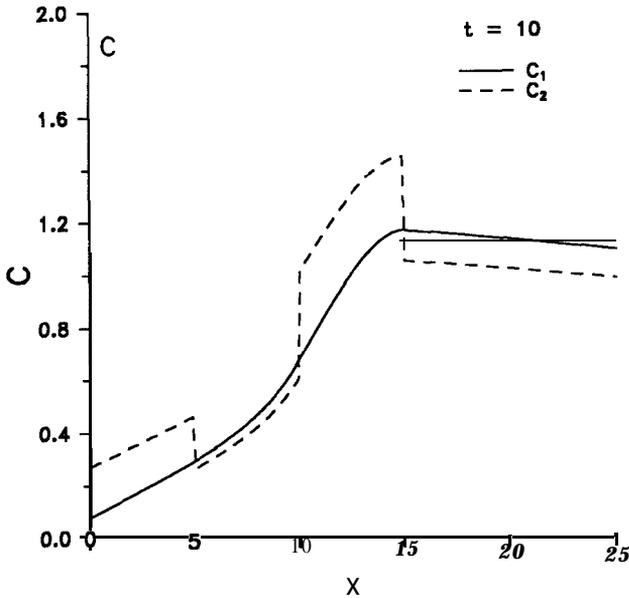


Fig. 7. (Continued)

A more detailed picture of the transverse solute profile as a result of non-equilibrium conditions is given in Fig. 6. This example illustrates a BVP involving the steady application of a solute to a circular region of the soil surface. Figures 6(a) and (b) give the C_1 and C_2 profiles, respectively, at $x = 10$ and $t = 1$. The highest concentration in the equilibrium phase in Fig. 6(a) occurs when non-equilibrium conditions dominate ($\beta = 0.1$ and $w = 0.1$). Note again that although these concentrations will occur in the effluent, concentrations in the soil expressed as solute mass per total liquid or bulk volume are considerably lower. Figure 6(b) shows relatively high values for C_2 during minor non-equilibrium conditions; in this case the solute transfers relatively easy from the equilibrium to the non-equilibrium phase because of the increased value of the transfer coefficient and a large proportion of the equilibrium phase. Figures 6(c) and (d) show transverse solute profiles for $t = 5$. The C_1 profiles are virtually identical and approach a steady-state profile for all three degrees of non-equilibrium. On the other hand, significant differences still exist between the C_2 profiles, with the non-equilibrium profile for $\beta = 0.1$ and $w = 0.1$ still slowly increasing. The difference in transverse profiles as a result of non-equilibrium is very similar as for the longitudinal profiles already investigated for one-dimensional transport (e.g. Toride et al., 1993). Eventually, all equilibrium and non-equilibrium profiles will become identical.

The last example deals with different Heaviside production profiles for the equilibrium and non-equilibrium phases. Figure 7(a) shows the assumed production profiles $\lambda_1(x)$ and $\lambda_2(x)$ in a semi-infinite rectangular area ($-\infty < y < 0$ and $-\infty < z < 0$). The equilibrium and non-equilibrium concentrations at $y = z = -10$ for $t = 1$ and 10 are given in Figs. 7(b) and (c), respectively. The non-equilibrium C_2 profile resembles the corresponding λ_2 distribution much more closely than the C_1 profile follows the λ_1 distribution. The explanation for this behavior is similar to that for the distributions in Fig. 4. The phase 2 solute profile is considerably less smooth than the phase 1 curve. Furthermore, the concentration below the production zone decreases as a result of dispersion. These observations hold true for the initial period ($t = 1$) as well as for $t = 10$, when a steady-state situation has been established in which the production and advection-dispersion processes balance each other.

Summary and conclusions

General analytical solutions were derived for three-dimensional non-equilibrium advective-dispersive transport during one-dimensional steady flow in a semi-infinite soil system. The transport model accounts for two-site chemical non-equilibrium or two-region physical non-equilibrium, and contains terms for first-order degradation, and zero-order production. The analytical procedure consisted of taking Laplace transforms with respect to time and the semi-infinite longitudinal spatial coordinate, and Fourier transforms for the infinite transverse directions. The inverse transformations were carried out according to procedures previously reported for one-dimensional non-equilibrium and three-dimensional equilibrium transport. The resulting general solutions of the BVP, IVP and PVP, apply to flux- and volume-averaged concentrations for phases 1 and 2. Solutions for a Dirac input or initial distribution could be readily derived from the general solutions. Other useful expressions were derived by specifying the transverse geometry where the solute was applied (BVP), initially distributed (IVP), or produced (PVP), namely: (1) a semi-infinite rectangle; (2) a finite rectangle; (3) a circle; (4) a sphere. Time-dependent solute input for the BVP was modeled as a series of step or Heaviside functions and an exponential function. The initial and production profile distribution were also specified vs. depth as Heaviside or exponential functions. For the Heaviside function this led to an initial or production domain that, corresponding to the previous four transverse geometries, consisted of a series of: (1) semi-infinite parallelepipeds; (2) finite parallelepipeds; (3) cylinders; (4) concentric shells. All specific analytical solutions were

presented in tabular form. Several graphical illustrations of concentration profiles and breakthrough curves were given for results obtained with solutions to the BVP, IVP and PVP. These results are generally straightforward extensions of previous findings for one-dimensional non-equilibrium transport.

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